MICROSTRUCTURAL AND CHEMICAL STUDY ON AN EXPANSIVE DOLOSTONE FROM ARGENTINA

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Abstract

An Argentinian fine-grained dolostone has proved to react deleteriously with alkalis following a mechanism similar to ACR. As this reaction is very controversial, the rock was reassessed for going deeper into the knowledge of its reactivity. The effect of the aggregate grain size on mortar expansion was evaluated by comparing RILEM AAR-2´s test results with those from Lu et al. test method. The inhibiting effect of a high-level replacement of low-calcium fly ash was also tested. The influence of rock porosity was studied on rock and concrete prisms, stored under conditions similar to ASTM C586 and RILEM AAR-3, respectively. Microstructural and chemical studies (mercury porosimetry, polarizing microscopy, XRD, SEM-EDS) were carried out on fresh and tested rock samples. The amount of alkali-silica gel observed was very low to explain mortar or concrete expansion. Fly ash failed to inhibit mortar expansion. The only correlation observed was between concrete expansion and degree of dedolomitization.

Keywords: alkali-carbonate reaction, dedolomitization, microstructure, porosity

1 INTRODUCTION

Alkali-carbonate reaction (ACR) is an unusual and harmful reaction that affects concrete durability and constitutes a subject of continuous debate among researchers and concrete technologists. Concrete structures affected by ACR have been reported mainly in Canada, USA and China [1].

ACR has distinguishing features: a) concrete expansion cannot be effectively controlled by using supplementary cementing materials, such as fly ash, for example, or by using lithium-based chemical admixtures [2]; b) the greater the maximum aggregate size, the greater the mortar or concrete expansion [3]; c) expansion of concrete is attributed to a dedolomitization reaction (forming calcite and brucite); however, there is much controversy about this particular issue [4].

In Argentina, there is a fine-grained dolostone that reacts deleteriously with concrete alkalis following a mechanism similar to ACR [5]. This rock clearly shows a dedolomitization process, but with no siliceous gel. Besides, the use of known mineral admixtures (fly ash, silica fume, ground granulated blast-furnace slag, natural pozzolan) or lithium compounds does not mitigate concrete expansion [6].

Considering that this reaction has always been very controversial, this particular Argentinian dolostone was reassessed in order to go deeper into the knowledge of its reactivity. The effect of the aggregate grain size on mortar expansion was evaluated by comparing the expansion results obtained by RILEM AAR-2 (formally RILEM TC 106-AAR [7]) with those from Lu et al. test method [3] (similar to RILEM AAR-5 [9]). This last test method was also run to evaluate the inhibiting effect of a high-level replacement of low-calcium fly ash. The influence of rock porosity was also studied on rock and concrete prisms, stored under conditions similar to ASTM C586 [8] and RILEM AAR-3 (formally RILEM TC 106-AAR [10]), respectively. Detailed microstructural and chemical studies (mercury porosimetry, water absorption and insoluble residue determination, polarizing microscopy, XRD, SEM-EDS) were carried out on fresh and tested rock samples.

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2 MATERIALS AND METHODS

2.1 Materials

Portland cements

Ordinary portland cements (type I according to ASTM C150 [11]), with high (1.1±0.1 % Na_2O_{eq}) alkali content (HAC), were used to make mortar and concrete specimens.

Valcheta Dolostone (VD)

The rock studied is a dolostone of hydrothermal origin (Lower Tertiary age), from Valcheta (Province of Río Negro, Argentina). It is a porous rock, composed of dolomite with a minor amount (1-2% modal) of detrital quartz, feldspar (some partially altered to illite) and fragments of rhyolitic rocks in a fine-grained matrix composed of clay (or clay-related) minerals. The grain size of the dolomite crystals ranges from 10 to 30 μm. The insoluble residue (IR) of the rock is variable (~3-18%) and according to previous XRD analyses [5, 12] it is composed of quartz, plagioclase (from the detrital fraction), illite, smectites and sepiolite (mainly in the matrix).

Two samples of this rock, with very different pore structure, were used throughout this study: a highly porous one (sample A) and a more compact one (sample B).

Fine aggregate

Non-reactive siliceous sand was used. This sand consists of fresh and unaltered quartz with minor amount of feldspar grains. It is a material of proved behavior and widely used for preparing control mixes in testing research in Argentina.

Fly ash (FA)

Low-calcium fly ash was used in this study for preparing mortar mixtures. It has low alkali content (1.5 % of Na_2O_{eq}) and a Blaine of 370 m^2/kg. As suggested by Lu et al. [3], the replacement used was 40 wt%.

2.2 Methods

General

The pore structure of Valcheta dolostone (samples A and B) was evaluated by mercury porosimetry and water absorption. The mineral composition and petrographic characteristics of this rock were assessed by complementary studies (insoluble residue, polarizing microscopy, XRD and SEM-EDS). In addition, several alkali reactivity test methods were applied on rock, mortar and concrete specimens in order to evaluate the expansive behavior of the rock samples under study and subsequently studied by polarizing microscopy, XRD and SEM-EDS. The main guidelines of these test methods are given below.

Mercury porosimetry, water absorption (WA) and insoluble residue (IR)

Porosity measurements on samples A and B were carried out with a Pascal 440 Thermo Fisher equipment (maximum test pressure: 200 MPa). WA and IR were measured according to ASTM C127 [13] and ASTM D3042 standards [14], respectively.

Polarizing microscopy

Thin sections (~20 μm thick) of fresh rocks and tested rock/mortar/concrete samples were studied by a Leica DM EP polarizing microscope (magnification of 15X-500X) in plane-polarized light (PPL) and cross-polarized light (XPL).

XRD

X-ray diffraction studies were performed on fresh rock samples (A and B) and on their IR. These results were compared with the mineral composition of the inner and outer zones of rock prisms after a 10-month alkali-immersion period. These studies were carried out using a Rigaku D-Max III-C diffractometer with Cu $K\alpha_{1,2}$ radiation (λ = 1.541840 Å) filtered with a graphite monochromator in the diffracted-beam, operating at 35 kV and 15 mA, with a 0.04 step and a counting time of 1 second per step. Glass holders were used.

SEM-EDS

Textural and chemical studies were performed on natural rock samples and mortar/concrete prisms (from Lu et al. and RILEM AAR-3 tests) using a Carl Zeiss high-resolution FE (Field Emission)-Σigma SEM microscope equipped with an EDS detector. Backscattered electron (BSE) images and compositional maps (Si, Al, Ca and Mg) were obtained working at 15 kV (at low

magnification) and 6 kV (at high magnification to enhance the contrast of the phases), specimen current of 0.1-0.2 nA, 20-30% dead time and $8x10^{-6}$ mbar vacuum. Samples were polished with alumina (abrasive size up to 0.3 μm) and carbon-coated. Compositional maps for other elements were not included due to their very low concentration (not showing discrete sectors).

Rock cylinder method

A modified version of ASTM C 586 [8] was applied in this study. Length changes were measured on rock prisms (25 mm x 25 mm x 50 mm) immersed in 1N NaOH solution at 23 °C (6 specimens per sample). The volume of alkali solution to the volume of rock specimen ratio was about 14. Rock specimens were drilled in random direction (bedding was not discernible).

Accelerated mortar bar test methods

RILEM AAR-2: 40 x 40 x 160 mm mortar bars were made with HAC, according to RILEM AAR-2 [7]. Mortar bar expansions were measured up to 30 days, maintaining the bars immersed in 1N NaOH solution at 80 °C.

Lu et al. method: 40 x 40 x 160 mm mortar bars were made with HAC and immersed in 1N NaOH solution at 80 °C, according to the method proposed by Lu et al. [3]. Mortar mixtures were prepared using an aggregate/cement ratio = 1 and a water-to-cement ratio (w/c) of 0.33. The grain size of the aggregate was between 4.8 mm and 2.4 mm. A high-range water-reducer admixture was used in order to adjust the workability of the mixture.

Mortar bar expansions were measured up to 30 days. Expansions greater than 0.10 % at 30 days are considered potentially deleterious. This test method was run to evaluate both the expansion response of the dolostone (sample A) and the effectiveness of FA for inhibiting the expansive reaction.

Concrete prism test method (CPT)

40 x 40 x 160 mm concrete prisms were made using the dolostone (A and B) as coarse aggregate (9.5 mm-maximum size) and non-reactive siliceous sand. Concrete mixtures were prepared with a cement content of 420 kg/m^3 and a high alkali loading (5.25 kg Na_2O_{eq}/m^3 of concrete), a coarse/fine aggregate ratio of 60:40 and a w/c of 0.45. The prisms were wrapped and put into sealed plastic bags, and stored at 38 °C [10]. Concrete expansions were monitored up to 1 year.

3 RESULTS

Samples A and B are mainly differentiated because of their contrasting porosity. Sample A is a highly porous dolostone (pore volume of 43.7 mm3/g, porosity 11.1%, average pore diameter 35.9 nm), with water absorption (WA) of about 5 % and IR of 6.1 %, while sample B corresponds to a more compact variety (pore volume of 3.4 mm^3/g, porosity 0.9%, average pore diameter 11.2 nm), with WA of 1 % and IR of 2.6 %. Although proportion of non-carbonated minerals is different in both samples, mineralogy of detrital particles and minerals in the matrix are the same. Petrography and XRD analyses in natural samples and their IR confirm the presence of quartz, plagioclase, illite, smectites and sepiolite as previously informed [5], and additionally some minor pyroxene and gypsum were identified in these samples. The absence of calcite in fresh samples was confirmed by XRD. Through SEM-EDS observations, the presence of laminar to massive hydrated Mg-silicates and Mg-aluminosilicates was confirmed surrounding dolomite crystals (more pronounced in sample A).

The results of the expansion tests are given in Table 1.

The expansive tendency of rock specimens is only evident for sample A, after 28 days of immersion in alkali solution. Although a large number of cracks was observed on the rock prisms, no typical signs of ASR, such as gel or stains could be seen. XRD studies show the presence of calcite and brucite in the inner zone of sample A (Figure 1a) and a major concentration in the outer zone with respect to dolomite (Figure 1b). As a result of its lesser porosity, sample B has no calcite or brucite in the inner zone of the specimens (Figure 1c) and only traces of these minerals in their outer zone (Figure 1d). Diffractograms (a) and (b) show low intensity peaks due to the low material sampled. Background elevation of the patterns is due to the glass holder signal.

AAR-2, AAR-3 and Lu et al. tests confirm the potential reactivity of sample "A", while sample "B" remains non-reactive (0.10% vs. 0.01% in the AAR-3 test respectively).

Petrography of concrete prisms made with sample B shows scarce and empty microcracks (up to 10 μm wide) in the paste or the cement-aggregate interface. In general, aggregates are unaffected (Figure2a), although some of them show slight signs of dedolomitization in their periphery (lighter rim) or inside the aggregate (Figure2b). Concrete prisms made with sample "A" show higher density

of empty microcracks (up to 10 μm wide) also in the paste or the cement-aggregate interface. In these samples, most of the aggregates show a dedolomitization process both in their periphery (lighter rim), and in the inner zone where this process is more accentuated (lighter core) (Figure 2c). Those evidences are more accentuated in mortar bars made with sample A and tested by Lu et al. method (OPC and OPC+40% FA), where more microcracks are detected and the lighter zones are not restricted to the rim or the core of the aggregate, but instead they define irregular patterns (non-concentric) (Figure 2d).

SEM-EDS analyses confirm those observations made by petrography. Concrete prisms elaborated with sample B show empty microcracks, and the dedolomitization process is restricted to a few particles. In those aggregates, dedolomitization was recognized in thin rims (up to 50 μm wide) and in localized sectors inside the particles. In concrete prisms and mortar bars made with sample A, microcracking and dedolomitization are more evident and pronounced. Only traces of alkali-silica gel were locally observed in cement-aggregate interfaces.

Different areas can be recognized in those aggregates with marked zoning from the cement paste to the inner zone of the aggregate (Figure 3 to 5). 1) Massive Ca-enriched sector (~ 5 – 10 μm wide) in the cement paste next to the aggregate (carbonate halo); 2) Thin sector (~ 6 μm wide) in the boundary of the aggregate enriched in laminar to massive Si-Mg-(±Al) phases with calcite and residual dolomite; 3) Thick sector (~ 100 μm wide) where dolomite grains with irregular boundaries predominate with surrounding Si-Mg-(±Al) phases and minor calcite; and 4) Inner zone (~ 2-3 mm wide) where calcite, brucite and Si-Mg-(±Al) phases and no dolomite were recognized. Details of these areas are shown in Figures 4 and 5. In addition, at "pore magnification" (1400 X) a thin zone enriched in Si-Mg-(±Al) phases can be observed between sectors 3 and 4 (Figure 3).

4 DISCUSSION

It is clear from the above results that sample A exhibits an expansive behavior as a result of the alkali attack, even though this rock does not reveal the texture and mineralogical composition typical of the alkali-carbonate reactive rocks.

The main difference between expansive (A) and non-expansive (B) samples is their pore structure: the more porous the rock is, the more expansive is its behavior (Table 1, ASTM C586 and AAR-3 tests).

Although smectites were recognized in the IR of the rocks, expansion contribution by clay minerals is unlikely (previous studies indicate negligible expansion and very low material loss by immersion in ethylene glycol [12]).

Even though the amount of the IR of the rock samples studied is moderated (~3 to 6 %), detrital fraction (quartz, feldspar and ryolithic rocks) represents only 1-2% (modal) of the rock. In addition, quartz does not show evidence of deformation and the glass content in the rhyolitic particles (<<0.01% of the rock) is very low. Although some release of silica from the detrital fraction and the minerals of the matrix should not be discarded, it does not justify the expansion measured in sample "A". Even though microcracks were clearly observed in mortar and concrete specimens, they are mainly empty, and the use of a high-level replacement of FA was not effective in controlling the expansion of the aggregate.

In contrast to what often happens on ACR aggregates [3], the expansion obtained with Lu et al.´s test method (2.5 mm to 4.5 mm) was barely higher than the one obtained with AAR-2 (0 mm to 4.5 mm). Nevertheless, this fact may be related with the high porosity of sample "A".

As new phases in the rocks, calcite and brucite were the main minerals recognized, supporting a dedolomitization process. Only traces of alkali-silica gel were recognized and additionally, new Si-Mg-(±Al) phases were detected inside the aggregate as a consequence of the alkaline attack, probably similar to that observed by other authors [15]. However, studies on these products and their formation mechanisms are in progress.

5 CONCLUSIONS

Although more samples should be analyzed, from the experimental results of this study, the following conclusions can be drawn:

- Dolostone from Valcheta can experiment different behaviors in alkaline conditions mainly depending on the pore structure of the rock. The more porous the rock is, the more expansive is its behavior.
- Although some release of silica from the detrital fraction and the minerals in the matrix should not be discarded, only scarce siliceous gels could be detected, and microcracks were generally

empty. In addition, 40% of fly ash could not inhibit the expansion process. Therefore, there is no strong evidence of ASR as an explanation for the expansion suffered by sample A.

- The only correlation observed was between concrete expansion and degree of dedolomitization (the greater the dedolomitization, the higher the expansion).
- The role played by the Si-Mg-(±Al) phases in the reaction process is under study.
- The irregular pattern of the dedolomitization attack observed on aggregates from sample A may explain the high dispersion measured in the rock prisms immersed in NaOH solution.

6 REFERENCES

[1] Ozol, MA (2006): Alkali-carbonate reaction. In: Lamond, JF, and Pielert, JH (editors): Significance of Tests and Properties of Concrete and Concrete-Making Materials, STP 169D, ASTM Int., PA (USA), Chapter 35: 410-424.

[2] Swenson, EG, and Guillott, JE (1964): Alkali-carbonate rock reaction. In: Proceedings, Symposium on Alkali-Carbonate Rock Reactions, Highway Research Record, HRTB, Washington, DC (45): 21-40.

[3] Lu, D, Fournier, B, Grattan-Bellew, PE, Xu, Z, and Tang, M (2008): Development of a universal accelerated test for alkali-silica and alkali-carbonate reactivity of concrete aggregates. Materials and Structures (41): 235-246.

[4] Jensen, V (2012): The controversy of alkali carbonate reaction: State of art on the reaction mechanisms and behaviour in concrete. In: Drimalas, T, Ideker, JH, and Fournier, B (editors): Proceedings, 14th ICAAR. Austin, Texas (USA), pp. 10.

[5] Milanesi, CA, Marfil, S, Batic, OR, and Maiza, PJ (1996): The Alkali-carbonate reaction and its reaction products - An experience with Argentinean dolomite rocks. Cement & Concrete Research (26/10): 1579-1591.

[6] Milanesi, CA, Marfil, S, Maiza, PJ and Batic, OR (2012): An expansive dolostone from Argentina – The common dilemma: ACR or another variant of ASR? In: Drimalas, T, Ideker, JH, and Fournier, B (editors): Proceedings, 14th ICAAR. Austin, Texas (USA), pp. 10.

[7] RILEM TC 106-AAR (2000): Detection of potential alkali-reactivity of aggregates – The ultra-accelerated mortar-bar test. Materials and Structures (33): 283-289.

[8] ASTM C586-11 (2012): Standard test method for potential alkali reactivity of carbonate rock for concrete aggregate (rock cylinder method). Annual Book of ASTM Standards (04.02): Concrete and Aggregates, ASTM Int., PA (USA): pp. 5.

[9] Sommer, H, Nixon, PJ, and Sims, I (2005): AAR-5 Rapid preliminary screening test for carbonate aggregates. RILEM TC 191-ARP: Alkali-reactivity and prevention - Assessment, specification and diagnosis of alkali-reactivity. Materials and Structures 38 (8): 787-792.

[10] RILEM TC 106-AAR (2000): Detection of potential alkali-reactivity of aggregates – Method for aggregate combinations using concrete prisms. Materials and Structures (33): 290-293.

[11] ASTM C150/C150M-12 (2012): Standard specification for portland cement. Annual Book of ASTM Standards, American Society for Testing and Materials. Annual Book of ASTM Standards, (04.01) Cement, Lime, Gypsum, ASTM Int., PA (USA): pp. 9.

[12] Milanesi, CA, and Batic, OR (1994): Alkali reactivity of dolomitic rocks from Argentina. Cement and Concrete Research 24 (6): 1073-1084.

[13] ASTM C127-12 (2012): Standard test method for density, relative density (specific gravity), and absorption of coarse aggregate. Annual Book of ASTM Standards (04.02): Concrete and Aggregates, ASTM Int., PA (USA): pp. 6.

[14] ASTM D3042-09 (2009): Standard test method for insoluble residue in carbonate aggregates. Annual Book of ASTM Standards (04.03): Road and Paving Materials, ASTM Int., PA (USA): pp. 4

[15] Katayama, T (2010): The so-called alkali-carbonate reaction (ACR) – Its mineralogical and geochemical details, with special reference to ASR. Cement and Concrete Research 40(4):643–675.

TABLE 1: Expansion of rock, mortar and concrete specimens.

Rock sample	Expansion (%)						
	ASTM C 586 rock prism (m: months)			AAR-2 at 28 days	AAR-3 at 12 months	Lu et al. at 28 days	
	1 m [1]	4 m [1]	10 m [2]			OPC	OPC+40% FA
A	-0.02 (0.01)	0.46 (0.40)	0.57	0.10	0.10	0.11	0.13
B	-0.02 (0.01)	-0.01 (0.00)	-0.02	-	0.01	-	-

[1] Average expansion of 6 prisms (In parenthesis: difference between maximum and minimum expansion values of rock prisms tested).

[2] Expansion of the rock prism assessed by XRD analysis.

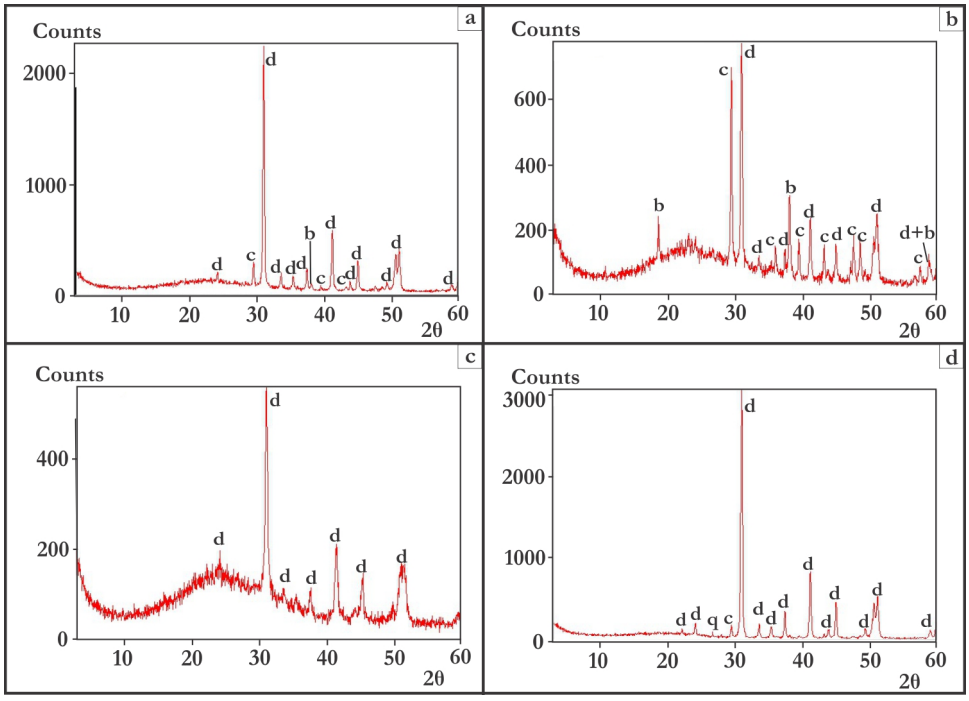

FIGURE 1: XRD of rock prisms after a 10-month immersion. Sample A: Inner (a) and outer (b) zones. Sample B: Inner (c) and outer (d) zones. d: dolomite, c: calcite, b: brucite, q: quartz.

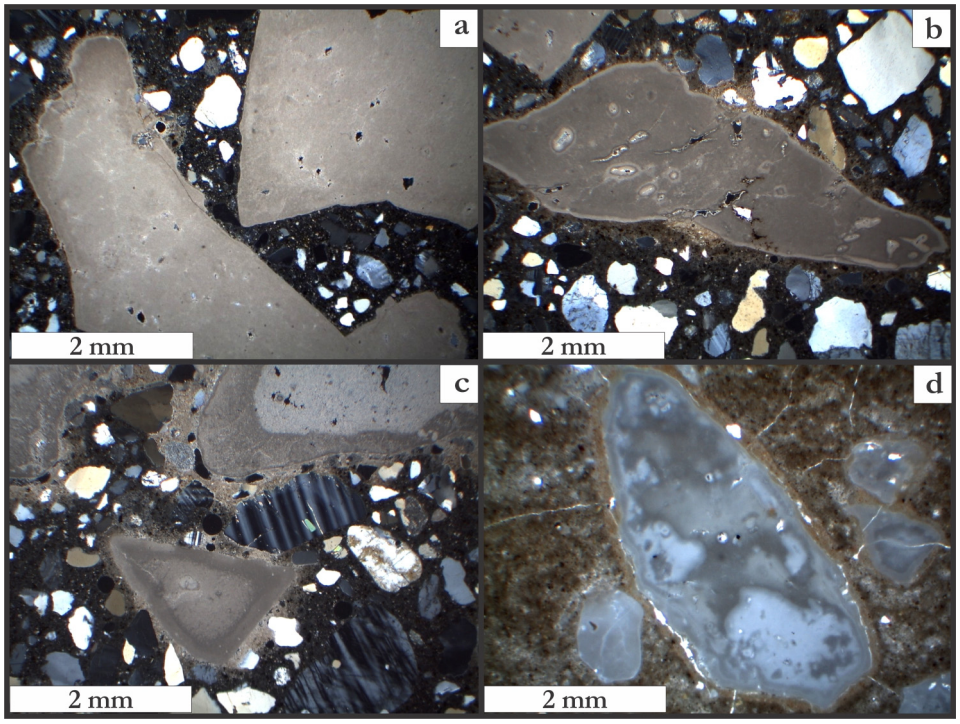

FIGURE 2: Photomicrographs (a-c: XPL, d: PPL). Sample B (AAR-3 test): Unaffected aggregates (a) and aggregate with slight dedolomitization (b). Sample A: Aggregates with strong concentric (c, AAR-3) and irregular (d, Lu et al. test) dedolomitization.

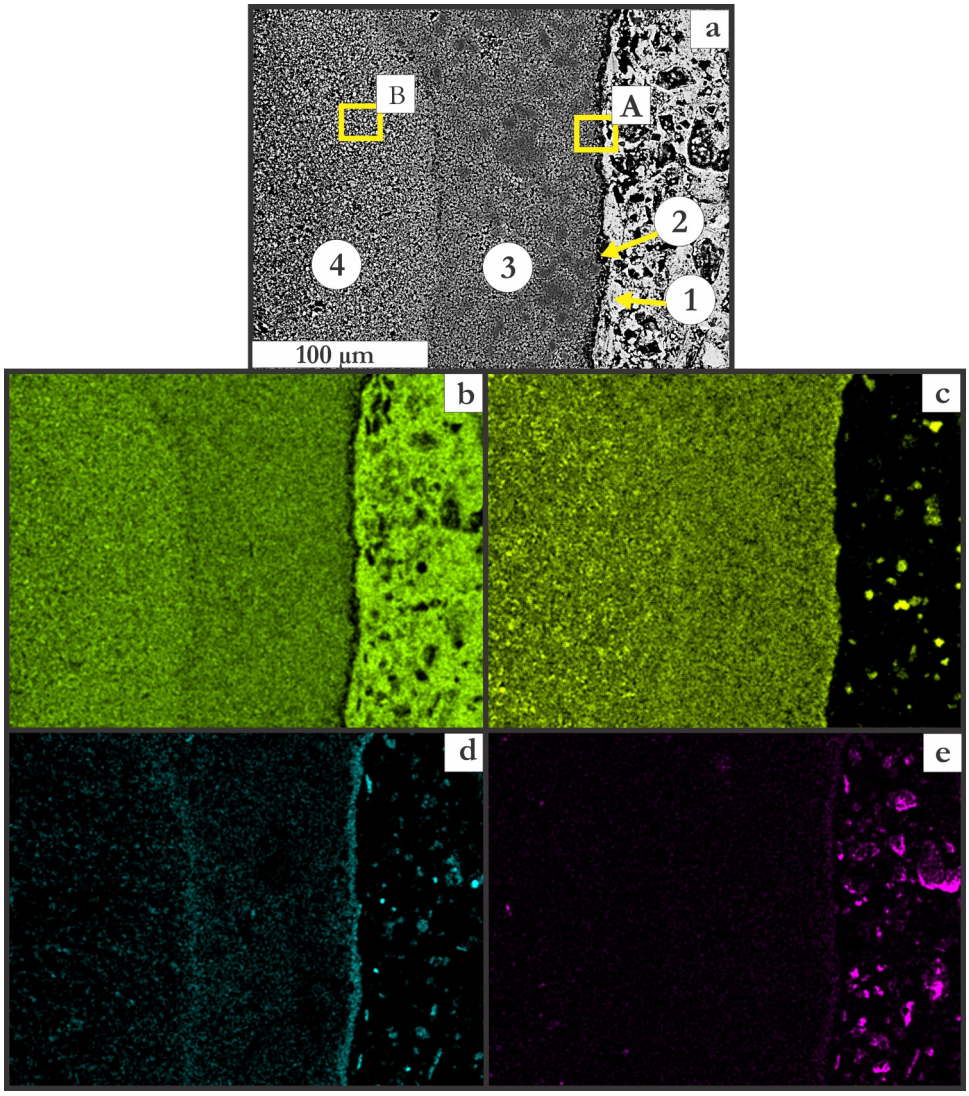

FIGURE 3: SEM-EDS. a) BSE image of an aggregate boundary in sample A (Lu et al. test). b-e) Compositional maps of Ca (b), Mg (c), Si (d) y Al (e) in the same sector. 1-4: Sectors described in text. A: Sector analysed in Figure 4. B: Sector analysed in Figure 5.

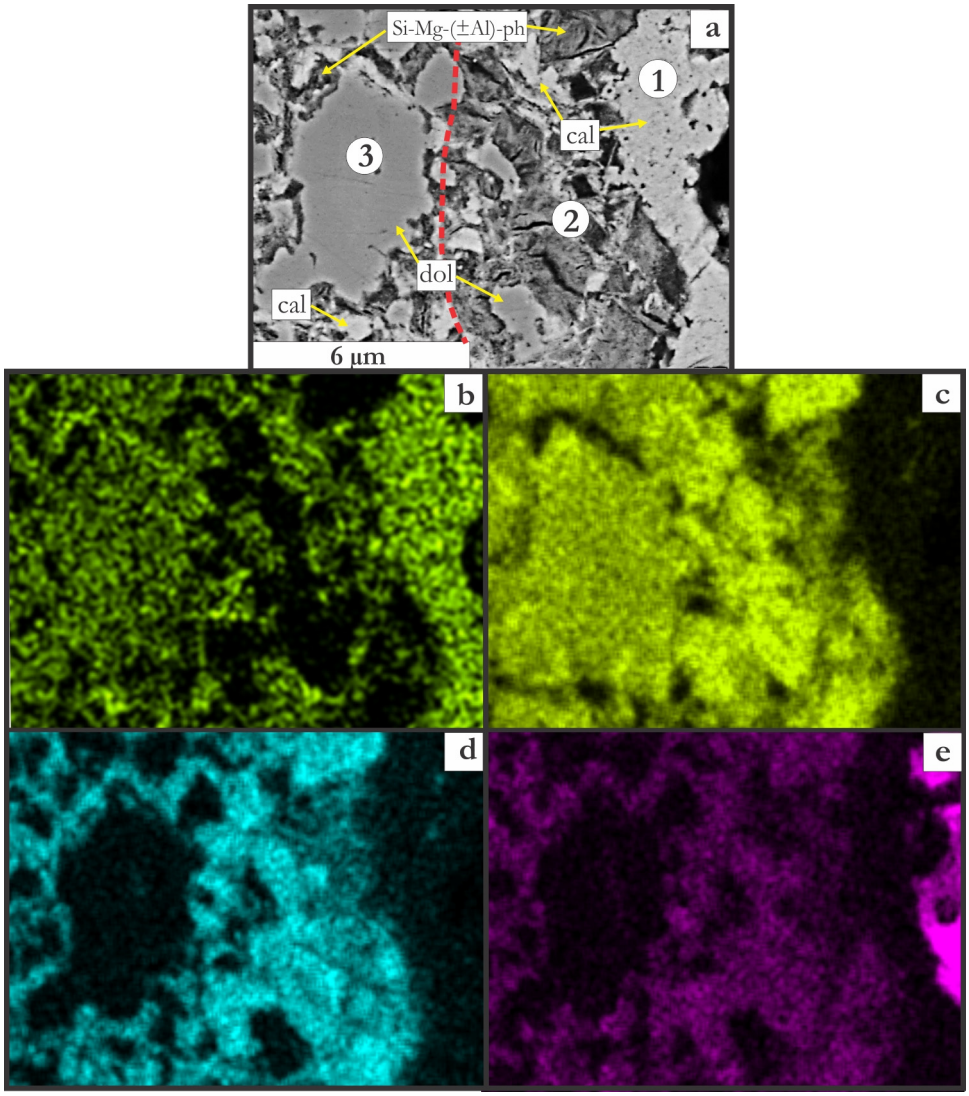

FIGURE 4: SEM-EDS. a) BSE image of sector "A" in Figure 3. b-e) Compositional maps of Ca (b), Mg (c), Si (d) y Al (e) in the same sector. 1-3: Sectors described in the text. dol: dolomite. cal: calcite. Si-Mg-(±Al)-ph: Si-Mg-(±Al) phases.

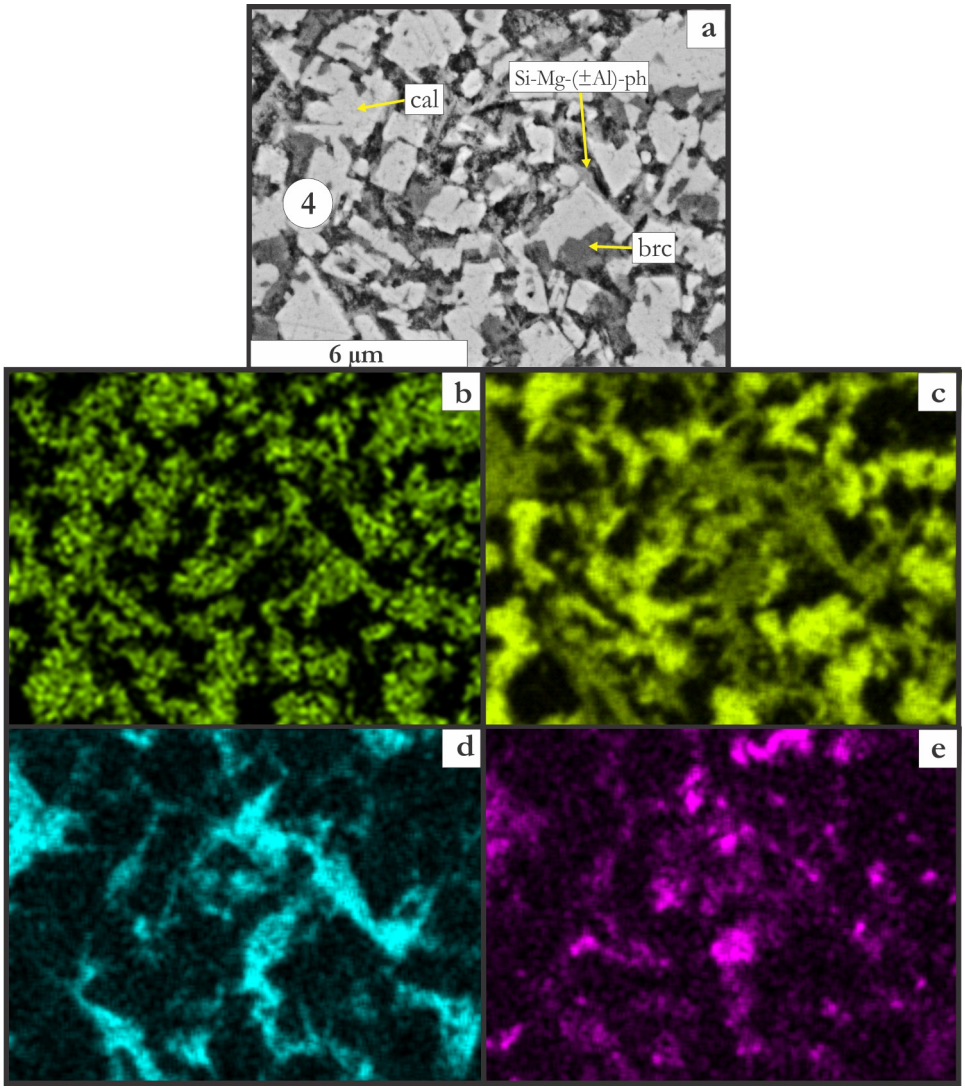

FIGURE 5: SEM-EDS. a) BSE image of sector "B" in Figure 3. b-e) Compositional maps of Ca (b), Mg (c), Si (d) y Al (e) in the same sector. 4: Sector described in the text. brc: brucite. cal: calcite. Si-Mg-(±Al)-ph: Si-Mg-(±Al) phases.